DATA ON THE FORMATION OF THE KAOLIN OF THE TOKAJ-MOUNTAINS

By J. MEZŐSI
Institute for Mineralogy and Petrography,
University of Szeged, Hungary

SUMMARY

In the southern part of the Tokaj-Mountains the kaolin and bentonite deposits are embedded in rhyolite-tuff-rhyolite of Tortonian-Sarmatian age. These have formed partly due to endogenic and partly exogenic process from orthohypomagmatites, pyroclastics and tuffits. While, in the case of the kaolinization of Végardó — Sárospatak and Mád may also be ranged here — the greater part of the basic rock is tuffit, at Bodrogszegi true pyroclasticum occurs. Here the action of the hydrothermae was the slightest, lasted the shortest time and the exogenic processes exerted their effect to the greatest extent.

Usually the formation-sequence of the mineral associations of the different deposits can be traced well. The changes of the pH can be well observed also in the occurrence of some of the characteristic minerals. The formation — sequence of the minerals corresponds to the observed one and it may also be characterised by the decreasing compound potentials.

The formation of the clay minerals has since a long time been of interest to investigators as well as to the parties concerned in ceramic and porcelain industry. As clay minerals from various ore deposits were investigated by different methods, the opinions concerning the formation differed also to a great extent. Besides the circumstances of the formation the starting rock plays also an important part. It is known that generally the feldspars and the glassy matrix of the tuffs and the acidic and to a smaller extent that of the intermediary and alkaline rocks compose the basis for the formation of the clay mineral. Hence, the clay minerals occur as secondary minerals. Both in the case of kaolinization and bentonitization regarding their formation the tracing of the weathering of the feldspars is an essential point of view.

The more important data of the literature referring to the kaolinization

On the basis of the examinations of *Correns* and *Engelhardt* [1939/40] the components of the feldspar dissolve as ions. The velocity of the weathering process increases with the decreasing grain-size and increasing temperature. Before the kaolinazition the lattice of the feldspar decomposes.

According to *Schiebold* [1931] at the weathering of the feldspars the alkalies on the surface of the lattice plane are in a very exposed situation, therefore, they dissolve easily. It has also been established that the presence of iron does not interfere with the kaolinization even Mn, Ca, Na, K only interfere if their total quantity related to that of Al_2O_3 does not exceed 0,02 : 1.

Frederickson [1951] states that at the weathering of the silicates in the first place at that of the feldspars the most exterior unbound oxygen ions of the silicate lattice attract one of the two free positive charges of the H_2O molecules, whereas the valency excess of the Al tetrahedrons is bound by the other free positive charge which in the feldspar was originally bound by K or Na.

Andreatta [1949] found that if the quantity of the water increases suddenly the minerals with a small compound potential dissolve first, whereas, of the minerals with a high compound potential, the elements of low ionic potential dissolve. Owing to this the weathering of the feldspars begins with the dissolution of the alkalies.

At many occurrence of hydrothermal clay minerals a zonal arrangement of them could be observed. According to *Sales* and *Meyers* [1948] the formation of the clay minerals is essentially simultaneous with the deposition of the ores, it is syngenetic and the development of the different zones may be considered as a reaction zone. From the original rock toward the hydrothermal vein the amount of Mg, Ca, Na and Si changes considerably.

Grim [1953] established that kaolinit may form both from acid and intermediary rocks, if at the weathering of the feldspars the alkalies and alkaline-earth metals disappear as quickly as they are released from the feldspar. The presence of Ca in the environment is not favourable for the formation of kaolinite.

Bates and Comer [1955] examined the weathering of the feldspars electron microscopically and found that on the cleavage plane of the microclin sometimes hexagons, which are probably kaolinites, may be detected.

At the weathering in addition to the sudden change of the water-amount, the pressure and temperature also change as compared to the conditions at the formation of the magmatic rocks, as it has been described in detail by *Szádeczky-Kaross* [1958—59]. Whilst the decrease of the pressure attempts to diminish the coordination number, the decrease of the temperature endeavours to elevate it. On the surface, the latter will play a considerable role. This change is particularly striking in the case of Al.

Stringham [1952] has summarised by the elaboration of the data of the literature the possibilities for the formation of clay minerals under hydrothermal conditions.

In order to elucidate the formation of the clay minerals many synthetic experiments have been carried out. Of these the experiments of *Noll, Gruner* and *Folk* are the most interesting.

The synthetic examinations of *Noll* [1935—1936] point to the fact that really speaking the formation of kaolin is a result of a very simple reaction, which takes place between Al_2O_3 and SiO_2 in the presence of water, i. e. kaolinization may occur both under hydrothermal and epigen conditions.

According to *Gruner* [1944] the conditions for the formation of the single clay minerals are determined by the concentration of the K ion as well as by the ratio of the Al_2O_3 and SiO_2.

Folk [1947] also states that the ratio of the Si: Al and the K content determines which mineral forms synthetically if the temperature and the pH are suitable.

THE CONDITIONS OF THE OCCURRENCE

Already since a long time investigators have dealt with the metamagmatites of the Tokaj-Mountains. While earlier principally the kaolinizaton of the extensive rhyolite-tuffs was taken into account recent investigations also the bentonitization of the rhyolite-tuffs have revealed. These recent investigations have shown that at the southern part of the Tokaj-Mountains there are four important kaolin occurrences: the kaolin deposit at Végardó, the occurrence in the northern vicinity of Bodrogszegi, the environment of the mine of Mount Bomboly in the eastern vicinity of Mád and the occurrence at Mount Megyer to the north of Sárospatak. Of these the occurrences of Végardó and Bodrogszegi will be dealt with in detail.

According to recent investigations the geological structure of the Tokaj Mountains is as follows. Tortonian rhyolite-tuffs with great gaps in the sedimentation settled onto Carboniferous and Triassic formations [*Pantó—Mrs. Széki—Fux,* 1959]. In the Sziget-Mountains of Zemplén situated in the vicinity, the same situation prevails [*Ferenczi,* 1943] Owing to the volcanic activity which started in the Tortonian a great deal of volcanic detritus has come to the surface. A part of these still fell into the shallow sea, which is also proved by the fossils found in them, in other places where the volcanic detritus accumulated in greater thickness true pyroclastic formed. After the andesite eruption succeeding it another rhyolite volcanic eruption followed in the Sarmatian producing both lava and tuff. Interesting data was obtained from a deep boring to the north of Sárospatak it opened up at a deepness of 225 meter, directly under the rhyolite tuff, Triassic limestone. According to the assumptions of *Vadász* and *Ferenczi* [1943] it composes a connecting link between the Sziget-Mountains at Zemplén and the Mountains of Szendrő-Rudabánya.

In the Tokaj-Mountains both the rhyolite tuffs and rhyolites of Tortonian and Sarmatian age are kaolinized and bentonitized. To separate them is mostly a very difficult task. Generally, however, the Tortonian formations are rather bentonitized and in the Sarmatian formations, more intensive kaolinization may only be found at the places where hydrothermal solutions exerted their action on these formations. The general kaolinization extending over the whole mountains is the result of an epigen effect.

Végardó

Frits [1955—1956] described the kaolin and bentonite deposit of Végardó. According to the fossils determined by *Schréter,* the kaolin and bentonite deposits opened up by drilling and underground mining are the alteration products of rhyolite tuff and rhyolite, respectively, of Sarmatian age. On the basis of present knowledge the kaolin deposit is the deepest. Over it there are three bentonite deposits interrupted by rhyolite tuff interdepositions. Occasionally the rhyolite tuffs and rhyolites are impregnated with pyrite. Pyrite appears in the form of very small crystals and its crystal shape is usually very simple.

The relatively fine granular composition of the kaolinous bentonitous deposit of Végardó is striking. The amount of the granules larger than 1 mm only rarely exceeds 10 per cent, mostly it is far smaller. Its greater part is rock fragments, angular and lobate quartz. The crystal fragments of quartz are never rubbed they have not been transported, occasionally their surface is corroded.

Fig. 1. Angular, lobated quartz fragment. Rhyolite tuff. Crossed nicols, x50.

The result of the mechanical analyses of some samples is shown in Fig. 2., accordingly the fraction not exceeding 0,25 mm usually ranges between 65—75 per cent. Although cases have occurred in which this fraction did not even attain 50 per cent, in these cases, howewer, it is shown by microscopical examinations the matrix is silicified to a smaller or greater extent distorting be original values of the grain-size.

In the case of several samples a fraction not exceeding 0,25 mm was cleaned. In almost 90 per cent of the cases the diameter of the grains of this fraction did not exceed 0,02 mm.

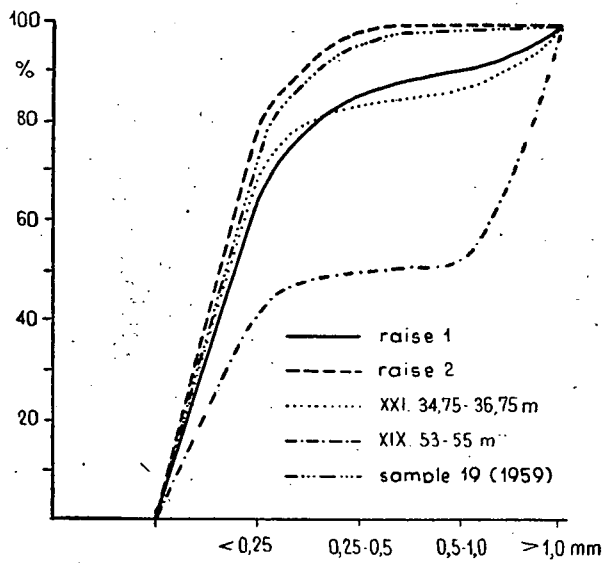

Fig. 2. Summary-curves of different kaolin samples from Végardó.

In the course of kaolinization an appreciable amount of silicic acid is released. Usually the released silicic acid separates as an opal. In the course of the weathering the silicic acid migrates towards the intact less decomposed rock. A good example for this is furnished by the occurrence in Végardó. At the raise of the subadit one finds in the lower part porous, pyritous in some places decomposed slightly kaolinized rhyolite-tuffs. Above the separation of the silicic acid appearing in a sharp line the tuff is strongly kaolinized it already belongs to the kaolin body. In this part the pyrite content is also minimal. The opaline part separating the two parts is 1—3 mm thick dark grey and sometimes permeated with pyrite veins. The pyrite veins run parallel to the opal zone and do not reach as far as the kaolin or the tuff part. Thus probably the pyrite contained in the opal is a syngenetic separation. The thinner and thicker opal veins can also be well detected under the microscope (Fig. 3.).

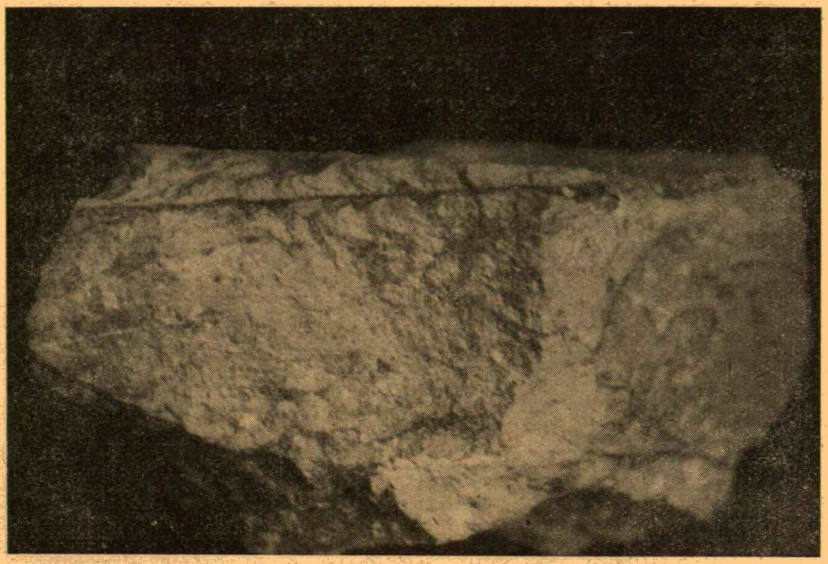

Fig. 3. Kaolinized and tuffaceuos part separated by an opal cord. $x^2/_3$

Another appearance of pyrite is also known when it appears in larger granules in the lower levels at the border of the kaolinized rhyolite tuff parts. On these chalcedony can always be found as one of the most recently separated minerals (Fig. 4.).

Fig. 4. Globular chalcedony on pyrite. x40

Kaolinite plays the most important role in the mineral composition of the kaolinized parts of Végardó. The DTA curve of the sample originating from the raise I of the A—73 levels has an ideal course. According to the examinations of *Földvári-Vogl—Koblenz* nakrite and dickite only appear in certain part in a subordinate amount and the

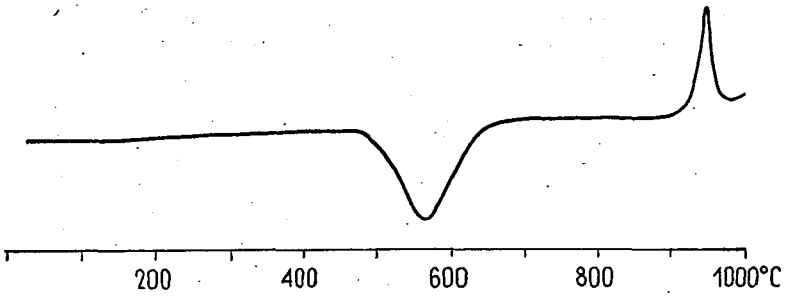

Fig. 5. The DTA curve of kaolinite from Végardó.

appearance is not connected with hydrothermae of high temperature. Their formation was more probably rendered possible through special conditions which are, however, as yet hardly known.

In some borings alunite also occurs. According to the chemical analyses the K_2O and Al_2O_3 content is high and the SiO_2 content is low. On the DTA curve besides the endothermic peaks characterising alunite the endothermic peak of the kaolinite also appears, thus between 500—600° C a double peak develops, the one appearing at lower temperature relates to alunite. For the sake of comparison the DTA curves of crystallized alunite of Beregovo as well as that of the mixture of this alunite with kaolinite from Végardó in a ratio of 1 : 1 were prepared. In the case of crystallized alunite at 570° C and 840° C

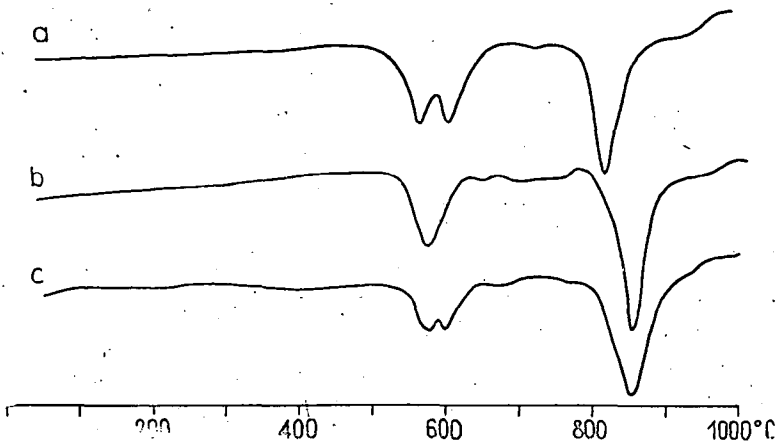

Fig. 6. a) Alunite with kaolin from Végardó, *b)* crystallized alunite from Beregovo, *c)* the DTA curve of a mixture of crystallized alunite from Beregovo and kaolinite from Végardó in a ratio of 1 : 1.

pronounced endotherm peaks appeare, at 620° C a smaller one, whereas at 750° C an exotherm peak can be found. On the DTA curve of the mixture mentioned above between 500 and 600° C the double peak developed and the endothermic peak appearing at lower temperature was coincided exactly with that of the alunite. At a little higher temperature the second endothermic peak appeared and disappeared the exothermic peak of 770° C.

According to *Kulp* and *Adler* [1950] the maximum of the first high endotherm peak appears around 550° C and the second around 810—850° C. Both denote a transformation of the lattice structure. At about 760° C a small exotherm peak appears pointing to the recrystallization of α Al_2O_3.

On examining the alunite-kaoline deposit at Beregovo, *Paluektova* observed [1957] on the DTA curves the first endotherm maximum at 590° C which means the disappearance of the structurally bound water and the second endothermic maximum at 845° C, when SO_3 group is released. At 765° she also observed a small exotherm peak.

In the case of the alunitous kaolin from Végardó the first endothermic peak also appeared at 600° C, the second one at 800° C. The exothermic peak only appeared in a blurred manner at no definite temperature and the exothermic peak of the kaolinite appearing between 900—1000° C, was also blurred.

The electron microscopical investigation also confirms the results of the DTA. The photos prepared from the suspension also give an

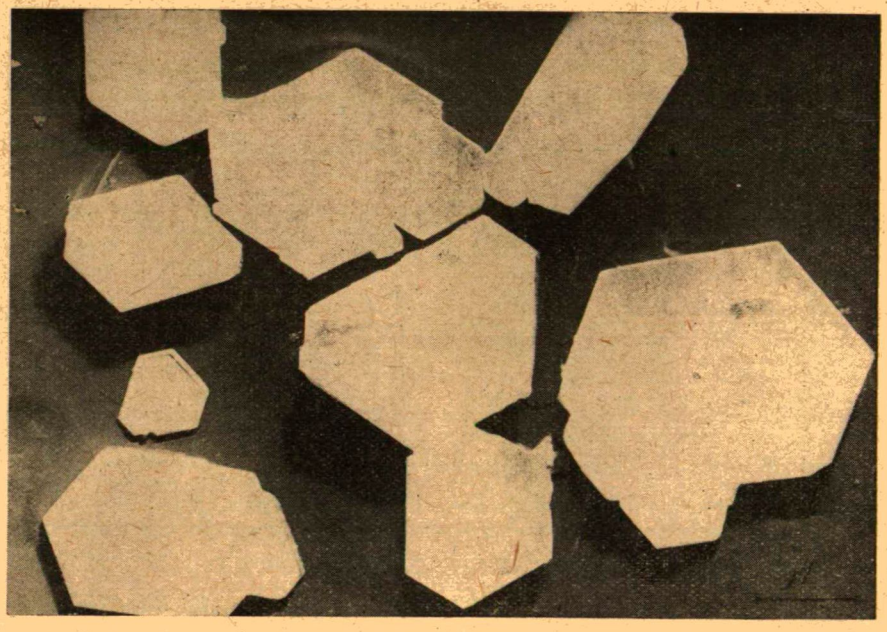

Fig. 7. Kaolinite crystals from Végardó.

ideal or slightly distorted picture of the kaolinite crystals. The size of the crystals is about 3 μ, whereas the thickness of the crystal plate calculated from the shadow is about 0,6—0,7 μ (Fig. 7.).

The photos are very interesting. The crystals are oriented arranged in such a manner as if the whole would be a single crystal. The edges are all parallel. The shadowings render well perceptible the pseudo-hexagonal plates of the kaolinite crystals. The size of the crystals varies, its measurable size lyes between 1—3 μ (Fig. 8.).

On the basis of the chemical composition of the kaolinized rocks and kaolins of Végardó the results of the analysis have been recalculated into elements which are summarized in the Table 1. The table also illustrates the trace elements.

Table 1.

	1	2	3	4	5	6	7
$Si^{4+} \cdot 10^2$	2171	2733	3368	3018	3332	3323	1485
$Al^{3+} \cdot 10^2$	1982	1436	941	1238	945	1054	1642
$Ti^{4+} \cdot 10^2$	10	20	29	29	27	17	17
$Fe^{3+} \cdot 10^2$	12	84	111	63	40	48	24
$Fe^{2+} \cdot 10^2$	—	1	7	—	tr	17	—
$Ca^{2+} \cdot 10^2$	9	14	20	23	25	20	31
$Mg^{2+} \cdot 10^2$	2	16	2	2	4	4	6
$Na^{1+} \cdot 10^2$	16	30	—	tr	tr	2	92
$K^{1+} \cdot 10^2$	24	30	6	tr	37	5	177
$P^{5+} \cdot 10^2$	13	7	—	13	8	—	—
$S^{6+} \cdot 10^2$	—	54	251	79	64	10	629
B	(tr)						(tr)
V							(tr)
Cr							(tr)
Co							(tr)
Ni							(tr)
Cu	tr						(tr)
Sn							(tr)
Pb	tr						(tr)
Mn	tr						(tr)?
As							(tr)
Si/Al	1,09	1,90	3,58	2,44	3,55	3,15	0,90
Al/Fe^{3+}	165,16	17,05	8,48	19,65	23,62	21,96	68,42
$K + Na \cdot 1000/Al$	20,18	41,73	6,38	0,81	39,15	6,64	163,82
K/Na	1,50	1,00	6,00	—	37,00	2,50	1,92

(tr)? — doubtful trace
(tr) — very weak line of spectrogram
tr — weak line of spectrogram

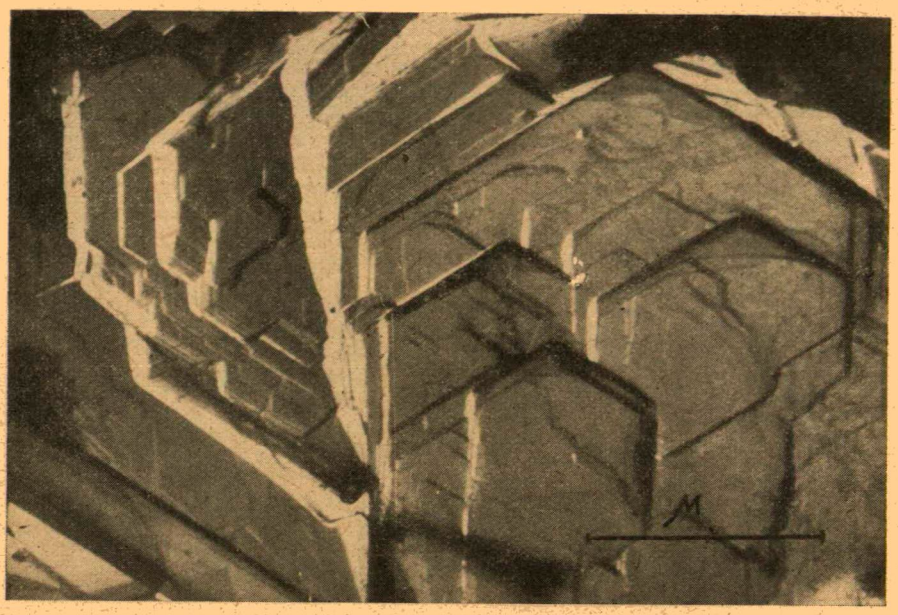

Fig. 8. Electron micrograph of kaolinite from Végardó prepared by the replica method.

Sampling places:

1. I. level, 1. raise 47,5—49,5 m,
2. three borings, the average of 59,03—76,43 meters,
3. boring No. IX, from 79,28—79,48 m, wtih much pyrite,
4. boring No. XIX. from 47—48 m,
5. boring No. XIX. from 48,5—51,0 m,
6. boring No. XIX. from 53,5—55,0 m,
7. boring No. XXI. from 34,75—36,78 m.

Of the results mainly the interpretation of the different quotients will be emphasised.

In the ideal kaolinite formula the Si/Al ratio is 1,04. Of the above values this is the most nearly approached by the substance obtained from the raise of level I which has also been proved by means of other examinations to be kaolin of a high quality. In the sample from boring XXI this value is only 0,9. This substance is, however, alunitized and the greater part of the Al is bound by this mineral. This is also de-

monstrated by the low Si value, thus a kaolin member containing more Al cannot be involved. In the other samples the Si/Al ratio is double or even triple, hence the substance is silicified which can also be observed under the microscope.

The Al/Fe^{3+} value shows the pureness of the kaolinite. The higher this number the more valuable the kaolin. A value about 20 still represents a good quality, decreasing values mean decreasing quality. Of the analyzed samples particularly the substance from the breaking out is very pure.

The $Ka + Na \cdot 1000/Al$ value shows really speaking the leaching factor. According to the examinations of *Laughlin* [1959] when the leaching increases and the weathering of the feldspars advances this value decreases also in the finer fractions. This is related to the fact that when the size of the granules decreases, the feldspar alters more easily, which has already been pointed out by *Correns* and *Engelhardt* [1939/40]. In the case of the above analysis this value ranges between wide limites showing the different extent of the kaolinization.

The base exchange possibilities influence somewhat the K/Na ratio, however, in the case of the kaolins it gives usually the ratio of the not weathered feldspars as in this case the cation exchange has a low value. In most cases, however, the decomposition of the feldspars is so great that the analyses either altogether do not contain alkalies, or only in a very insignificant percentage.

In the above analyses the FeO content is very minimal often it is lacking which proves that the weathering of the rock, the process of kaolinization took place under oxidative conditions.

The examinations of the minor elements show that the hydrothermae related to the hypovolcanites contain copper and lead in traces. A part of the copper and lead is bound to pyrite. As, however, these two elements only appear with a very weak spectogram line, their greater part can be found in the kaolinized parts, where these two components show a weak spectogram line. According to the examinations of *Laughlin* [1959] the V, Cr and Sn presumably substitute the iron in the octahedral layer. The Co and Ni give a very weak spectogram line. Ca and Mg appear in all cases with a strong spectogram line. Of the sedimentophil elements only B appears is very weak traces. It is interesing that Au, Ag, Bi, Zn, Zr, Be and Ge could not be detected. In the pyrite besides the Cu and Pb only As appeared with an averagely strong line, the Mn and Sb are questionable. Thus this pyrite is fairly pure and approaches the ideal composition.

The hydrothermae breaking up also at present are bound to fault lines. Their composition is fairly uniform. Hydrocarbonatous — sulphatous waters dominate in which Ca and Na are the dominating and Mg the subordinated cations. In small amounts iron may be found. The pH value is generally about 7. The thermal water break up from a depths of 70—90 m. Apparently the kaolinized-bentonitized zone plays the role of a water closing layer. At present their temperature does not exceed 30° C.

Table 2 shows the chemical composition of the hot waters.

Table 2.

	1		2		3		4		5	
	mg/l	equ. %	mg/l	equ. %	mg/l	equ. %	mg/l	equ. %	mg/l	equ. %
Na	219,6	41,99	202,5	38,48	218,0	41,73	360,2	65,93	341,5	66,95
Ca	194,3	42,64	200,3	43,68	196,7	43,21	99,0	20,85	97,4	21,91
Mg	42,1	15,23	47,7	17,14	41,6	15,06	31,1	10,79	24,8	9,19
Fe	—	—	3,5	0,55	—	—	16,0	2,42	12,0	1,94
ammonium	0,6	0,14	0,6	0,14	tr	—	tr	—	—	—
Cl	88,4	10,97	87,6	10,79	89,8	11,15	89,4	10,64	82,8	10,53
H_2CO_3	472,3	34,02	488,1	34,94	474,7	34,23	530,8	36,70	469,8	34,70
SO_4	600,8	55,01	596,3	54,26	596,0	54,62	599,2	52,66	583,4	54,77
NO_3	—		—		—		tr		—	
meta silicic aoid	19,5	—	28,6	—	28,0	—	—	—	5,2	—
free carbonic acid	—	—	138,6	—	129,3	—	156,4	—	81,1	—
total dissolved salt	1637,6		1793,8		1774,1		1882,1		1698,0	
alkalinity	7,74				7,78		8,70		7,70	
total hardness	36,90				37,12		21,03		19,33	
carbonate hardness	21,67				21,78		24,36		21,56	
O_2 consumption mg/l					1,6					

Places of water sampling:

1. from raise from subadit
2. boring 22. at the end of the subadit
3. boring IX/1. 88,09—88,59 m
4. boring XI. 76,0—77,9 m
5. boring XII. 82,1 m.

The hydrothermae are very uniform. This is also well illustrated by the diagram (Fig. 9.). Perhaps only the water breaking out from borings IX/1 and XI shows some difference namely the Ca and Mg is lower and the Na content higher. The anions, however, are present in the same amount. It is also characteristic of these waters that they contain a fairly appreciable amount of free carbonic acid.

At the investigation of the origin of the kaolin-bentonite deposit of Végardó it may be assumed that the rhyolitic volcanic fragments fell into the sea at the beginning which on the action of the sea water started to diagenese. The higher pH of the sea water, as well as the fact that the alkalies dissolved created a suitable physico-chemical environment for the beginning of the decomposition of the feldspars of these tuffs and tuffits, respectively, i. e. for the beginning of the leaching of the alkali content of the binding substance of the tuffs.

Later the hydrothermal solutions breaking out in connection with the hypomagmatits brought about the pyrite impregnation which can be seen in certain places in the rhyolite tuffs. At the weathering of the pyrite with plentiful solvent in an oxygen rich environment — these occur in the oxidation zone — an environment with a low pH developed on the action of sulphuric acid. The low pH value, the potassium

free and oxygen rich environment made the kaolinization possible. This was particularly favourable along the fault lines quite close to the hydrothermae. If there also occurred a part of tuff in which the feldspar did not decompose completely the movement of the solutions was fast enough to remove the dissolved alkalies and that finally kaolin should form.

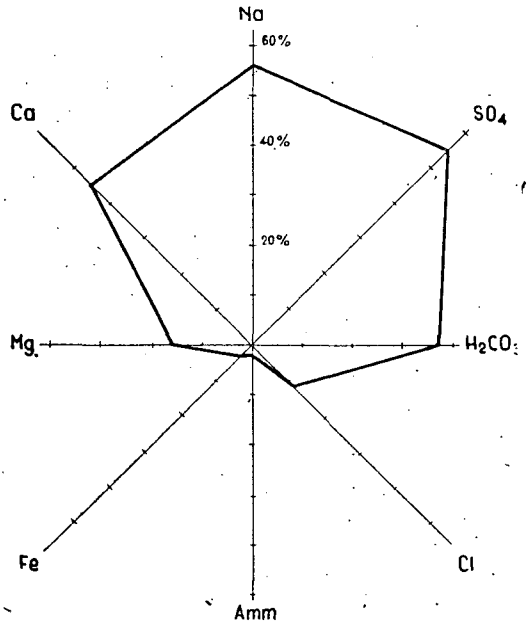

Fig. 9. The chemical composition of the hot water of Végardó.

Taking the above into account the formation of the minerals occurs probably in the following sequence. After the bentonitization of the early tuffits following the appearance of the hydrothermae, i. e. in a certain respect simultaneously with it, first kaolinite appeared associated in some places with alunite. The lacking of halloysite and allophane point to the fact that at the formation of the deposit epigen processes did not play an essential role. Although these form at a low pH value the temperature must have also been very low. With the advancing of the weathering of the residual feldspars and with the solution of the potassium and sodium content of the binding substance of the tuff the pH value of the solution gradually increased. For dickite to form either a higher temperature, or greater pressure or some other specific condition is needed. The fact that this mineral is present in a subordinated amount shows that all these circumstances were lacking. Usually nacrite forms at a lower temperature this is also supported by the fact that it often occurs together with cinnabar. In the southern part of the Tokaj-Mountains Hg does not even appear as trace element. Apparently for the formation of nacrite too quite specific conditions are required.

Regarding the appearance of alunite the question of the role of

potassium arises. The changing of the acidity is favourable for the weathering of the feldspars from where potassium may be dissolved, but in such cases it is also favourable if the glassy component in the rock contains potassium. Potassium may also be dissolved from deeper layers. In the deposits this must all be taken into account. It is, however, a fact that the amount of K may have been quite insignificant which is demonstrated by the local appearance of alunite and the complete lacking of illite.

The appearance of the calcite shows that the pH value of the solutions rises slowly and has shifted towards the alkaline region. However, it did not increase to such an extent for the physico-chemical conditions to be suitable for the formation of zeolite.

The lacking of the illites proves that the potassium needed for their formation was already removed when the environment would have become suitable for their formation.

The passages of the breaking out hot water solutions are bound to fault lines thus of course, the most intensive kaolinization will be found along these lines. The kaolin bodies with irregular shapes will form along them. The formation of the bentonite deposits is not unfailingly bound to the fault lines their greater part forms from tuffite of rhyolite, respectively.

Bodrogszegi

In rhyolite tuff of Sarmatian age stocklike kaolin occurrences with about a 200 m long trend and 30—50 m wide at about a depth of 25—50 m are known as has been recently described by *Frits* [1956]. The geological position of the formation is not yet quite elucidated. The underlaying rock is formed of pumicestone rhyolite tuffs with a »stone powder« texture. Perlite and obsidian lapillies varying in colour occur in it. It hardly contains any coloured minerals. In the vitreous binding substance splintered quartz crystal fragments may be detected. Generally the tuff is finely granular and the deposite is not divided.

The substance of the kaolin body is fairly uniform and the finely granular substance is permeated by limonitic manganic veins (Fig. 10.).

The rhyolite tuff is boundered by quite irregular surface. In some places swelling outs can be observed. Both the kaolin and the bordering tuff part is irregularly and networklike permeated by a light brown substance which is merely contaminated kaolinite stained with limonite and fireclay, respectively. This can also be proved by the fact that if this substance is pulverised, the iron may easily be dissolved with diluted HCl and a yellow white substance remains, the DTA curves of which show the curves characterizing these substances. Between the kaolin body and the tuff, in some instances in the kaolin body too, there are sliding planes which are sometimes brown coloured. Under thermicroscope in the matrix of the tuff appendixlike formations could be found which proved to be kaolinites. They disintegrate easily into smaller fragments vertically to their longitudinal axis, hence they can only form locally because they do not bear any transport.

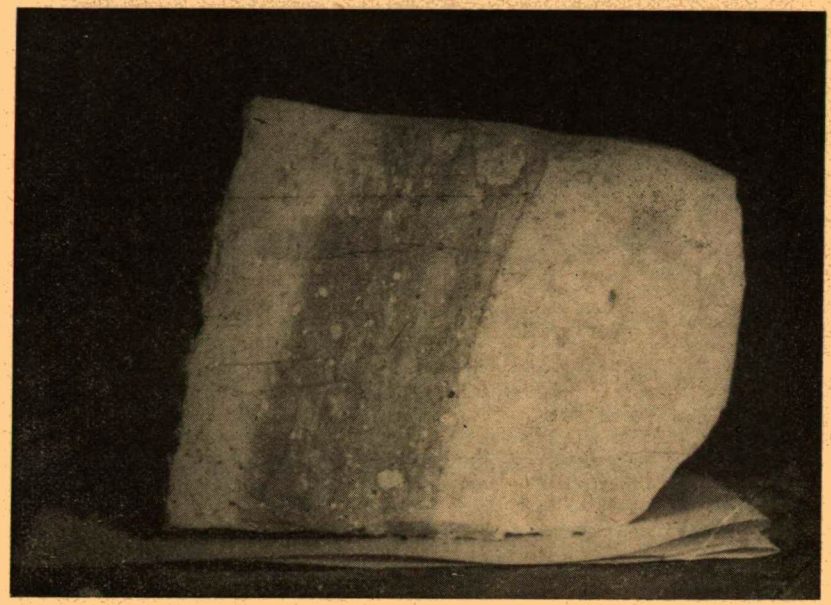

Fig. 10. Kaolin stained with limonite bands.

The grain-size analysis of the substance of the kaolinbody furnished the following result:

Table 3.

	0,25 mm ⊘	0,25—0,5	0,5—1,0	1,0
V. level, SE part	87,50 %	7,31 %	0,48 %	4,71 %
V. level, SW part	73,80	24,16	1,74	—
V. level, S part	94,20	3,10	2,70	

In detail the grain-size analysis shows that the size of those not exceeding 0,02 mm amounts to about one quarter of the substance, hence the mechanical analysis also supports the fact the substance contains very many colloidal fractions and that the single samples do not contain fractions exceeding one mm in diameter.

Just in the case of the minerals belonging to the kaolin group the DTA examinations do not give an unequivocal result. The examinations show that the substance surely contains kaolinite this is also proved by photomicrographs and electronmicrographs. The differentiation of halloysite and fireclay by means of DTA is doubtful owing to the nearly identical dehydration sections. In the curves the endotherm peaks between 100—200° C developing a different manner, generally they appear between 130—140° C which is according to the data of the literature characteristic of fireclay. The DTA examinations of the country rock only show an endotherm peak at about 570° C which characterizes kaolinite, whereas the exotherm peak is only weak (Fig. 11.).

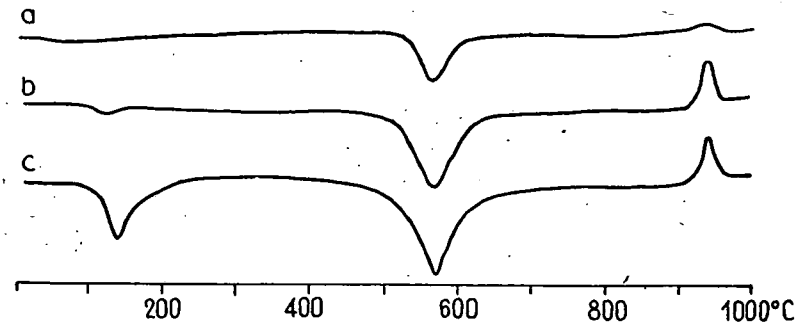

Fig. 11. a) The DTA curve of the country rock of the kaolin body.
b) The DTA curve of the substance of level IV.
c) The DTA curve of the substance of level V.

To identificate the substance exactly, Debye-Scherrer diagrams were prepared from the substances of various levels and fractions.

Table 4.

1		2		3		4		5		6	7	8
d (kx)	I	d	I	d	I	d	I	d	I	d	d	d
7,3	vw	7,33	9			7,24	10	7,3	7			
4,9	vw			7,04	8					7,15	7,17	7,17
4,46	w									4,455	4,455	4,47
		4,315	10	4,370	10	4,370	10			4,35	4,36	
								4,16	10			
4,18	vw									4,17		
3,59	w	3,568	8	3,601	8	3,592	6	3,602	7	3,566	3,57	3,577
3,38	vw									3,365		
		3,277	4	3,284	6							
								3,191	4			
								2,995	2			
2,76	vw									2,748		
2,64	w											
		2,511	8	2,528	10	2,540	6	2,515	6	2,521	2,50	
		2,457	5									
2,35	w	2,319	8	2,320	10	2,324	6	2,315	6	2,331	2,325	2,336
								2,175	1	2,182		
2,01	vw											
		1,973	3	1,9855	5	1,9805	1	1,9473	3	1,985	1,977	1,985
				1,8000	4			1,8312	2	1,835		
		1,783	1							1,778	1,785	1,786
1,693	w									1,682		
		1,660	6	1,6615	8	1,658	5	1,6692	4	1,659	1,659	
		1,6126	2	1,608	2					1,616		
		1,5304	2	1,531	3					1,539	1,541	1,538
1,496	w									1,486	1,486	1,485
		1,4785	8	1,4720	10	1,4735	7	1,4754	6	1,464		1,455
		1,4445	2	1,4395	2					1,449		
1,293	w	1,3656	3	1,3656	4							1,372
		1,2755	4	1,2765	6	1,2758	4	1,2802	3			1,2847
1,242	w											1,2476
		1,2288	4	1,2306	6	1,2242	3	1,2270	3			

The data of the exposure of the X-ray diagram:

1. Fe Kα without filter, 30 kV 12 mA.
2, 3, 4. Co anticathode, Fe filter, 23 kV, 32 mA.
5. Cu anticathode, Ni filter, 27 kV, 4,2 mA.

The samples were taken from the following places:

1. Bodrogszegi, V. level, original powdered substance,
2. Bodrogszegi, V. level, original powdered substance,
3. Bodrogszegi, V. level, a fraction of 0,002 mm of the previous substance,
4. Bodrogszegi, V. level, a fraction not exceeding 0,002 mm,
5. Bodrogszegi, IV. level, a fraction not exceeding 0,002 mm,
6. Kaolinite values obtained by *Brindley* and *Robinson,*
7. Fireclay values obtained by *Brindley* and *Robinson,*
8. Fireclay values obtained by *Robertson, Brindley* and *Mackenzie.*

On comparing the values concerning kaolin and fireclay reported by *Brindley* and *Robinson* [1951] and by *Robertson, Brindley* and *Mackenzie* [1954] with our data relating to fireclay, in both cases the values are in fairly good agreement. The fact that the kaolinite values relate to the well crystallized kaolinite explains why in this case relatively fewer lines appear. In addition some lines refer to the presence of feldspar and quartz. The lacking of well crystallized kaolinite is shown by the absence of the very characteristic lines 4,17 and 4,12. The 2,32 *d*-value referring to the fireclay appears in most of the samples very intensively.

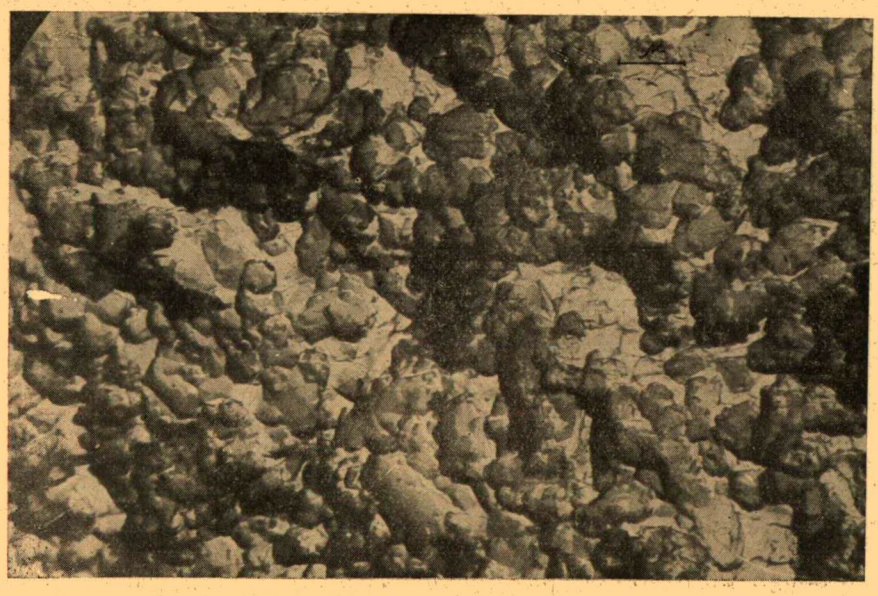

Fig. 12. Electron micrograph of the substance from level V prepared with the replica method.

The evaluation of the X-ray data also only shows that beside kaolinite fireclay is certainly present. However, the colloidal character is demonstrated by the fact that the lines are fairly wide and in some cases blurred. It is also striking that the very intense lines are nearly all lacking. Hence the substance is only composed of weakly crystallized kaolinite and fireclay.

The electron micrographs, at least those relating to the substance of level V, exclude halloysite. On the replica photos distorted hexagonal formations pointing to kaolinite can only rarely be seen. However, it may very well observed that the substance contains many colloidal fractions consequently globular-rheniform forms appear (Fig. 12).

Table 5. illustrates the data of the chemical composition recalculating the analytical results to elements and the minor elements.

Table 5.

	1	2	3	4	5	6
$Si^{4+} \cdot 10^2$	2276	2144	2661	2156	2160	1996
$Al^{3+} \cdot 10^2$	1670	1746	1312	1797	1778	1692
$Ti^{4+} \cdot 10^2$	11	7	6	7	6	13
$Fe^{3+} \cdot 10^2$	194	213	147	201	206	197
$Fe^{2+} \cdot 10^2$	13	6	24	10	10	—
$Mn^{2+} \cdot 10^2$	2	4	4	3	2	6
$Mg^{2+} \cdot 10^2$	10	—	—	—	2	2
$Ca^{2+} \cdot 10^2$	14	13	34	16	14	25
$Na^{1+} \cdot 10^2$	7	7	32	8	7	25
$K^{1+} \cdot 10^2$	42	32	213	31	31	26
$P^{5+} \cdot 10^2$	3	2	1	2	2	7
$S^{6+} \cdot 10^2$	—	—	—	—	—	3
B						(tr)
Cu						tr
Pb						tr
Si/Al	1,36	1,23	2,03	1,20	1,21	1,19
Al/Fe^{3+}	8,61	8,19	8,93	8,94	8,63	8,48
$Na + K \cdot 1000/Al$	29,34	22,34	186,74	21,70	21,37	30,50
K/Na	3,00	4,57	6,66	3,87	4,43	1,04

The occurrences of the samples:

1. Boring II. 28,3—31,7 m,
2. Boring II. 43,9—47,3 m,
3. Boring II. 63,0—66,4 m,
4. Boring II. 72,6—75,3 m,
5. Boring II. 81,9—84,1 m,
6. Paperkaolin.

Although the coloured rock-making minerals do not play an essential part in the rock, yet the relatively high value of Fe^{3+} is striking. This high iron content is also demonstrated by the fact that limonite

often stains the kaolin in stripes this can be particularly well observed on the V. level of the South-Western area. In this part manganese minerals are not present they may rather be found on the part in the vicinity of the tuff. In the places where manganese minerals occur the kaolin is nearly quite pure, the manganese compounds are concentrated in small groups, whereas the compounds containing iron mostly stain the kaolin yellow.

The chemical composition of the substance is fairly uniform. This holds good too for the parts which are also worked at present and for the substance of the borings. According to the analytical data the Si/Al ratio is generally higher than ideally in the case of the kaolin.

The $K + Na \cdot 1000/Al$ value shows the amount of the feldspar which remained intact. At the measuring of the grain-size it was revealed that the greater part of the substance from Bodrogszegi can be suspended. In the suspension most of the grains belong to the clay fraction. If it is taken into account that this factor diminishes with grain-size its low value may be understood. But for one exception the values are approximately identical which means that the kaolinization is about uniform in the whole deposit.

Under certain conditions the potassium sodium ratio indicates the relation between two different feldspars. In view of the fact that the kaolin minerals have a low adsorption capacity the potassium and sodium can only originate from the not yet weathered feldspar and to a smaller extent from the glassy pumice-stone binding substance. The ratio generally exceeds one, showing that the sanidine content of the altered rock is also in the present state larger than the amount of the plagioclases, i. e. the potassium content of the binding substance is higher than that of the sodium.

According to *Robertson, Brindley* and *Mackenzie* [1954] who have dealt in detail with investigation of kaolinite and fireclay chemical calculations have shown that in the fireclay type in the tetrahedral layers the substitution of the $Si \rightarrow Al$ is the double of that in kaolinite and the members of the kaolin groups with a regular structure in general. While on the one hand, in the tetrahedral layers such differences can be distinguished in the various types, on the other hand, in the octahedral layer such differences cannot be found in the substitution. In our case this could not be established because pure substance was not available thus the amount of colloidal silicic acid is not known and a decision wether or not there is Al in excess could be reached.

The minor element-associations show a very scanty picture. Of the chalcophil elements only Cu and Pb appear in traces and of the sedimentophil ones only B is present with a very weak spectral line. Whilst the amount of Cu and Pb ranges between 0,01—0,001 per cent, the amount of B does not exceed 0,00001 per cent, it is, therefore, quite insignificant.

The occurrence of fireclay in the Tokaj-Mountains is not extensive in kaolins it can only be found here. On the basis of the data of

the literature fireclay is a mixture of the refractory clay minerals. So it appears in Pilisszentiván where the parent-rock of the refractory clay containing fireclay is probably an lateritic sediment. In the refractory clay from Cserszegtomaj also occurs the kaolin of the fireclay type. In this case the kaolin and bauxite formations are probably due to the same substance. Only the different physico-chemical conditions altered the environment and rendered possible the associated occurrence of the two formations.

Robertson, Brindley and *Mackenzie* [1954] established that the crystals from Pugu irregular arranged in the direction of the *b* axis are morphologically very perfect. They believe that the cation exchange capacity is rather due to the tetrahedral and octahedral positions than to the valencies of the crystal edges. In the deposit of Pugu migmatite and gneiss are the original rocks. The irregular kaolin crystale arranged according to axis *b* represent together with a finely granular quartz and feldspar sand a deeper sea facies.

In Bodrogszegi the formation conditions were different. The appearance of the andezite volcanity rendered the keeping open of the lines possible to this the formation of a cleavage structure following the orogenic movements contributed too. According to the traces along the fault lines very weak hydrothermal solutions broke out at a very low temperature. This process could, however, not be permanent, which is also proved by the fact that although the feldspars decompose, the residue is usually composed of colloidal substances X-ray analyses and electron micrographs also demonstrate this. The kaolinite present also demonstrates that epigen effects play an essential role at the formation. The appendixlike kaolinites are very weakly crystallized. The appearance of colloidal substance in larger amounts suggests that the hydrothermal solutions only play a greater role at the decomposition of the feldspars. The weak crystallinization of the kaolinites furthermore, the presence of fireclay prove that epigen effects played a great role in the formation of the deposit. Te pH value of the circulating solutions was throughout low as minerals, on the basis of presence of which a greater fluctuation of the pH might be assumed, could not be found.

Concerning the formation of the fireclay all data emphasise the great role played by the epigen conditions. In this case, therefore, according to the above this must primarily be taken into account, i. e. the hydrothermal solutions only performed the breakdown of the feldspar and the transport of the released ions. The formation of the new minerals is mostly due to epigen effects.

The continental origin of the transformed tuff is also proved by the absence of the montmorillonites which are represented in the vicinity in fairly large amounts and furthermore, that no layers can be detected in the tuff. The absence of illites points to the fact that the pH value of the solutions did not change appreciably during the transformation furthermore, that during this period the circulation of the solutions was also good and the K ions were transported as a whole.

Szádeczky-Kardoss refers to the fact that in the magmatic processes the liquid magmatic section composes as compared to the resudual magmatic phase a separate system. The separation sequence of the rock-making minerals also shows decreasing compound potentials. In the residual solutions on the basis of the decreasing compound potentials. It the residual solutions on the basis of the decreasing compound potentials a sequence may also be established which also corresponds on the whole to the formation sequence. Hence, both at the crystallization of the solutions as well as at the mineral associations formed on the action of the hydrothermal solutions decreasing compound potentials are obtained. After the liquid magmatic phase suddenly another series showing a decreasing compound potential starts. At the weathering the experimental sequence of the secondarily formed clay minerals can also be ranged according to the decreasing compound potentials.

Using the ion and anion potential values of *Szádeczky-Kardoss—Grasselly* [1959] the minerals forming at the alteration due to the hydrothermal solutions may be ranged according to the decrease of their compound potential:

Table 6.

minerals	composition	compound potential
Or-adular	$KAlSi_3O_8$	0,72
quartz	SiO_2	0,71
kaolinite	$Si_3AlO_{10}Al_4(OH)_8$	2,07
	$Si_4O_{10}Al_4(OH)_8$	2,06
alunite	$KAl_3(OH)_6(SO_4)_2$	2,02
illite	$KAl_2Si_4O_{10}(OH)_2$	1,94
montmorillonite	$Si_8O_{20}(OH)_4Al_3Mg$	1,91
beidellite	$Si_8O_{20}(OH)_4AlFe_3$	1,87
nontronite	$Si_8O_{20}(OH)_4Fe_4$	1,79
calcite	$CaCO_3$	1,42
baryte	$BaSO_4$	1,03

Of course, these compound potential values were calculated from a simplified formula not taking into account the substitution possibilities although there are wide possibilities for the substitution in the case of the phyllosilicates on the one hand in the tetrahedral layers, which in most cases means a Si — Al substitution, and on the other in the octahedral layers between Al—Mg, Al—Fe^{3+} etc. The above compound potential values show clearly that the members of the montmorillonite group, apart from the extreme values, succeed illite and kaolinite.

The values of the above table can be plotted in a coordinate system where on the one axis the approximate pH intervals and on the other the ψ values are shown. The succession is well visible.

At the formation of these minerals the change of pressure is not essential as the process occurs on the surface or near it. The change of temperature must already be taken into account, however, this also ranges between relatively small limits, usually it decreases gradually. Concluding from the minerals formed and from the present temperature of the solutions there has not occured any considerable change in

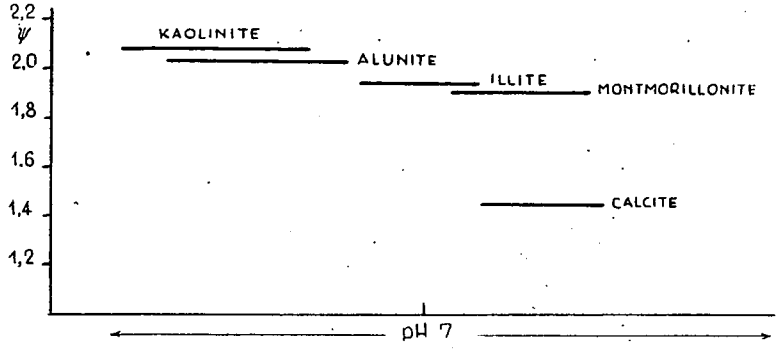

Fig. 13. The mineral association of Végardó as a function of ψ and pH.

their temperature in the Tokaj-Mountains it ranges between 200—230° C. Only the change in the concentration of the solutions was significant. The pH value increased gradually from 2—3 to about 8—9. Thus, at the development of the types of the different minerals the change in the concentration and in the pH played the most important role. The decreasing compound potential values quasi indicate what possiblities existed under the given conditions at the formation of the different minerals. The rare occurrences of beidellite and nontronite may be explained by the fact that in some cases it was not possible that besides the other conditions of the formation iron should also be present in considerable amounst.

The succession of the minerals separating from the solution can be characterized by the Bowen series. In this case the compound potential values show a decreasing value. The orthoclase and quartz, however, separating at the end show an appreciably lower value than the kaolinite or alunite forming first on the action of hydrothermal solutions. The series of the minerals forming after kaolinite is a series according to a decreasing compound potential into which apart from the clay minerals both calcite and baryte, but even chalcedon, fit.

Szádeczky-Kardoss demonstrates in the case of the magmatic processes two separate systems, the compound potential values of which also differ distinctly from each other. The one is the liquid magmatic phase and the other the residual-magmatic phase. The clay mineral series forming secondarily on the action of the hydrothermal solutions again shows a sudden change in its compound potential thus from that point of view this is a third phase. Like in the postmagmatic phase in this case also a great amount of solvent is present and the concentration of the ions is very low.

Taking the Si/Al ratio of the decreasing values of the above compound potentials into account, beginning from the kaolinite towards illite and montmorillonite the ratio gradually shifts and the amount of the Si gradually increases. In this series too like in the Bowen series the decreasing compound potential value indicates an increasing degree of silification. This is well illustrated in Fig. 14.

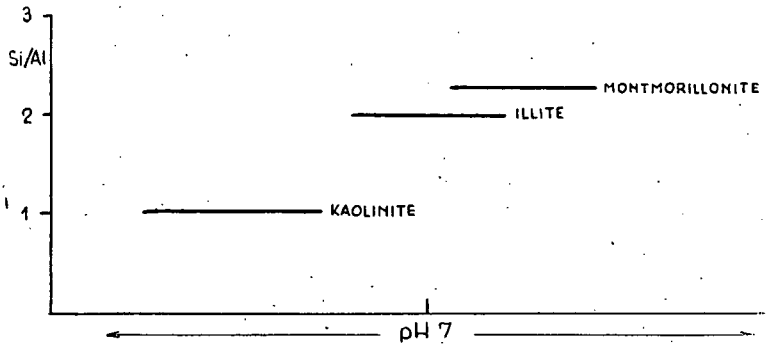

Fig. 14. The Si/Al ratio of clay minerals as the function of the pH.

In the examined cases the kaolins of the Tokaj-Mountains are poor in minor elements. The kaolinites from Mád, Bodrogszeg, Sárospatak and Végardó characteristically only contain Cu and Pb. The alunite occurrence of Végardó is an exception as in it V, Cr, Co, Ni, Sn, Mn, and As also appear in traces. Pyrite also only contains few minor elements. The purity of the spectrum demonstrates that both the pyrite appearing crystallized and the pyrite in opal is an epigen formation. The compound potential value fits well into the series of the clay minerals. As according to *Szádeczky-Kardoss* two compounds can only crystallize together if their compound potential is similar, the fact that pyrite also forms after the clay minerals may be explained on the basis that its compound potential is far lower than the one of kaolin, besides other circumstances this also points to the fact that these two minerals cannot be syngenetic.

The theory concerning the above sequence of formation of the clay minerals is also in agreement with the examinations of Korshinsky. According to him the acid components of a solution (CO_2, HCl, H_2S etc.) penetrate far quicker into a rock than the other components of the solution. In aqueous solutions the acid components have an ion mobility which is greater on the average than that of the alkaline components. Particulary the H ion is far more mobile than the OH one. Hence, it may be assumed that the acid components the ascendent solutions penetrate far more quickly upwards than the alkaline components. Consequently the acidity maximum of the postmagmatic solutions must be less deep, in abyssic depth this condition shift towards the alkaline region. This is the reason why in greater depths sericite, and in higher regions kaolin, take the place of feldspar.

This is also expressed by the establishment of *Szádeczky-Kardoss* concerning the volatiles. According to him in not great depths only the most light volatiles, water, CO_2 and sulphur originating from organic substances exert a transvaporisation action.

ACKNOWLEDGEMENT

The electron mierographs were prepared in the Electron Microscopic Laboratory of the Academy in Moscow. The chemical analyses were made in the Hungarian State Geological Institute. The roentgenograms were prepared by *M. Matherny* in the Institute for Mineralogy and Petrography of the Technical University of Bratislava and by *G. Bidló* and *T. Mándy* in the Institute for Mineralogy and Petrography of the Technical University of Budapest. The examinations of the minor elements were partly carried out by *I. Kubovics* in the Institute for Mineralogy and Petrography of the Eötvös Loránd University of Budapest and partly by *F. Pintér* in the Institute for Experimental Physic of the University of Szeged.

The author expresses his gratitude to them.

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